Comparative Shock-Tube Study of Autoignition and

Plasma-Assisted Ignition of C$_2$-Hydrocarbons

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The kinetics of ignition in C$_2$H$_2$:O$_2$:Ar, C$_2$H$_4$:O$_2$:Ar, C$_2$H$_6$:O$_2$:Ar and C$_2$H$_5$OH:O$_2$:Ar mixtures was analyzed in experiments using a shock tube with a discharge cell. Ignition delay time was measured behind a reflected shock wave after a high-voltage nanosecond discharge and in its absence. Numerical simulation was used to show the main mechanisms that lead to peculiarities of ignition properties of C$_2$-hydrocarbons.

1. Introduction

In recent decades particular attention had been drawn to applications of non–equilibrium plasma for plasma–assisted ignition and plasma–assisted combustion (PAI/PAC) [1-3]. It was shown experimentally and numerically that nanosecond discharge plasmas have profound effect on ignition delay reduction and flame stabilization in various combustible mixtures.

It is interesting to compare ignition of hydrocarbons under the same conditions when hydrocarbon molecules contain the same number of C atoms. This has been done for oxidation of C$_2$H$_6$, C$_2$H$_4$ and C$_2$H$_2$ by measuring the induction period in shock waves in thermally-equilibrium regime [4]. In this work, using observations in a shock tube with a discharge cell, measured ignition delay times were compared for stoichiometric and lean C$_2$H$_6$-, C$_2$H$_4$-, C$_2$H$_2$- and C$_2$H$_5$OH-containing mixtures both in autoignition regime and ignition with non-equilibrium plasma. Ignition delay was studied after a high-voltage nanosecond discharge and in its absence. We measured ignition delay time in a lean C$_2$H$_6$:O$_2$:Ar mixture and in lean and stoichiometric C$_2$H$_4$:O$_2$:Ar mixtures. The obtained results were compared with our previous studies of ignition of C$_2$H$_6$ [5], C$_2$H$_2$ [6] and C$_2$H$_5$OH [7]. Numerical simulation was used to analyze ignition properties of C$_2$-hydrocarbons with and without non-equilibrium discharge plasma.

2. Experiment

Shock tube technique has been widely used to measure autoignition delay times in combustible mixtures. In this work, to show the effect of discharge plasma, ignition in C$_2$-hydrocarbon–containing mixtures was studied in a shock tube after the discharge and in its absence. Non-equilibrium plasma was created by a high-voltage nanosecond discharge. Gas mixtures under study were heated by a reflected shock wave just before discharge initiation. In this experiment, the discharge processes occurred on a nanosecond scale, whereas ignition developed at times longer than tens microseconds. Chemically active particles were formed in the discharge plasma to favor the ignition at gas temperatures above self-ignition threshold.

A detailed description of the experimental setup and methods used to study PAI has been given elsewhere [8-10]. Observations were made in the shock tube (25×25-mm^2 square cross section) with a 1.6 m long low-pressure channel and a 60 cm long high–pressure chamber. The stainless–steel channel had two pairs of windows for optical diagnostics. In addition, the Plexiglas discharge section of the shock tube had eight optical windows made of quartz or MgF$_2$. The metal end plate of the tube served as a high – voltage electrode, whereas another electrode was the opposite grounded steel section of the tube.

Ignition was studied in a lean (φ = 0.5) C$_2$H$_6$:O$_2$ mixture and in stoichiometric (φ = 1) and lean (φ = 0.5) C$_2$H$_4$:O$_2$ mixtures (10%) diluted with Ar (90%). Ignition delay time was measured behind a reflected shock wave. In this region, the gas temperature was between 1100 and 1700 K and the corresponding pressure was between 0.3 and 0.7 atm. The values of gas pressure and temperature behind a reflected shock wave were obtained from the analysis of the data on initial mixture composition, initial pressure, and measured velocity of the incident shock wave.

Shock wave velocity was measured with three laser Schlieren systems installed along the shock tube. Ignition delay time was defined as the time interval between the Schlieren signal on the reflected shock wave arrival at the diagnostic cross
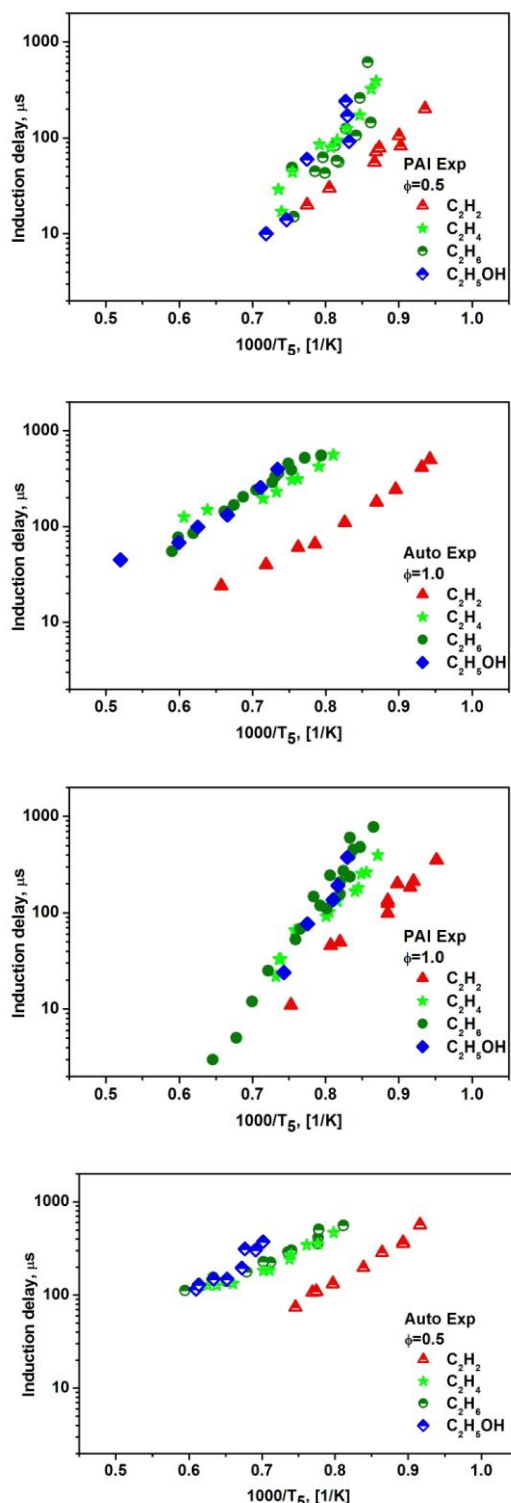
Fig. 1. Comparison of measured induction delay times for autoignition (auto) and plasma-assisted ignition (PAI) of C_2-hydrocarbons for different equivalence ratios.

section near the endplate and the onset of the leading front of the CH emission at 431 nm. To study the effect of discharge plasma on the ignition, a high – voltage discharge was initiated at the instant when the reflected shock wave reached the diagnostic cross section. The total time of plasma

generation and decay was much shorter than the delay times for autoignition and PAI. Indeed, the composition of the dominant active species produced in the discharge reached their quasi-steady values in the discharge afterglow in ~ 0.5 μs, whereas the ignition delay time under the conditions studied was in the range 10 - 300 μs. This allowed a separate consideration of excitation kinetics and ignition kinetics.

Fig. 1 compares new measured data on delay times for autoignition and plasma-assisted ignition in C_2H_6- and C_2H_4-containing mixtures with our previous measurements for ignition of C_2H_6, C_2H_5OH and C_2H_2. Additional nonequilibrium excitation leads to a strong reduction in the ignition delay time. The effect is more profound for higher gas temperatures at which the specific deposited discharge energy is higher.

The data shown in Fig. 1 were obtained using the same setup and for the same range of gas parameters. Therefore, this comparison shows peculiarities for autoignition and plasma-assisted ignition in the C_2-containing mixtures under study. The data obtained for C_2H_6, C_2H_4 and C_2H_5OH are close to each other, whereas the delay time for autoignition and plasma-assisted ignition in C_2H_2 that is highly reactive are much shorter. The autoignition delay time is independent of the equivalence ratio in the C_2H_6- and C_2H_4-containing mixtures, whereas this time in the C_2H_5OH- and C_2H_2-containing mixtures is shorter for the stoichiometric mixtures than that for the lean mixtures. In plasma-assisted ignition, the delay time is approximately the same for $\varphi = 1$ and 0.5 in the C_2H_4 and C_2H_2 mixtures; in contrast, the induction times in the lean C_2H_6- and C_2H_5OH-containing mixtures are shorter than those in the stoichiometric mixtures.

3. Numerical simulation

To show the main mechanisms that lead to peculiarities of autoignition and plasma-assisted ignition times for C_2-hydrocarbons, ignition in the mixtures under consideration was numerically simulated with and without the additional excitation by the discharge. We studied the temporal evolution of the mole fractions of chemically active species in the discharge, in its afterglow and in the ignition phase. The method and kinetic schemes used to simulate the discharge phase and discharge afterglow have been described in detail elsewhere [5, 10]. Ignition processes were simulated on the basis of the kinetic scheme for autoignition [11]. Ignition delay time was calculated from the analysis

of the time evolution of CH mole fraction in the ignition phase. This approach allowed good agreement between our previous measurements and calculations for autoignition and plasma-assisted ignition of CH_4-C_5H_{12} [5, 11], C_2H_2 [6] and C_2H_5OH [7].

Fig. 2 compares ignition delay times calculated in this work for autoignition and plasma-assisted ignition with the measured data in C_2H_4-containing mixtures. Agreement between the calculated and measured results for autoignition and plasma-assisted ignition is good. It is better for the lean mixture and for lower gas temperatures when the specific deposited energy per one neutral particle is lower.
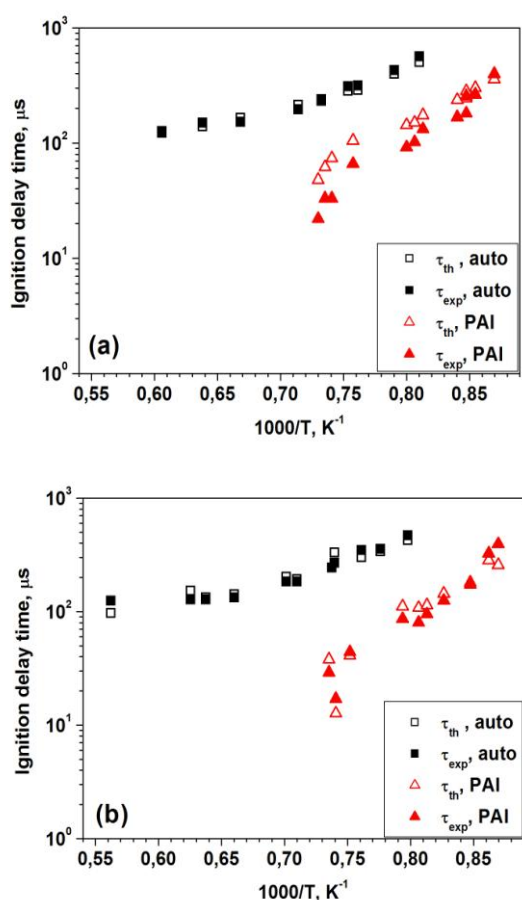

Fig. 2. Ignition delay times for $\phi = 1$ (a) and $\phi = 0.5$ (b) ethylene mixtures during autoignition and PAI. Closed symbols correspond to measurements and open symbols correspond to calculations.

Fig.3 demonstrates the difference in dominant ignition processes for various C_2-hydrocarbons. Sensitivity analysis was made for the autoignition and plasma-assisted ignition in the stoichiometric C_2H_2:O_2:Ar(a), C_2H_4:O_2:Ar(b), C_2H_6:O_2:Ar(c) and C_2H_5OH:O_2:Ar(d) mixtures at the same values of initial gas temperature and pressure. The value of

energy deposited in the discharge also was fixed and equal to 0.05eV/particle. The rate coefficients of every pair of forward and reverse reactions were in turn increased by 50% and the ignition delay time was calculated in each case. The sensitivity coefficients, $(\tau_i - \tau_0)/\tau_0$, were again calculated, where τ_0 is the ignition delay time calculated with unchanged rate constants and τ_i is the ignition delay time calculated with the increased rate constants for the i-th pair of forward and reverse reactions.

We analyzed the calculated results for the reactions when the magnitude of the ratio $(\tau_i - \tau_0)/\tau_0$ was higher than 0.05 at least for autoignition or ignition by the discharge. The sensitivity analysis showed the most limiting reactions and led to the following conclusions. For all C_2-hydrocarbons, the $H + O_2 \leftrightarrow O + OH$ reaction always exhibits the greatest sensitivity (20-40% decrease in the ignition delay time) both for autoignition and for ignition after the discharge. This chain-branching reaction leads to an increase in the amount of radicals and is generally important in ignition of different fuels at T > 1100 K.

Ignition of C_2H_2 and C_2H_6 is controlled only by three and six chemical reactions, respectively, that significantly affected the ignition delay. The number of reactions that greatly affect ignition of C_2H_4 and C_2H_5OH is several times higher. All dominant reactions for the ignition of C_2H_2 lead to a reduction in the ignition delay time when increasing their rates. For other C_2-hydrocarbons under study, many reactions lead to a reduction in the ignition delay time when increasing their rates, whereas some other reactions have an opposite effect on ignition.

4. Conclusions

Using a shock tube with a discharge cell, ignition delay time was measured in a lean ($\varphi = 0.5$) C_2H_6:O_2:Ar mixture and in lean ($\varphi = 0.5$) and stoichiometric C_2H_4:O_2:Ar mixtures with a high-voltage nanosecond discharge and without it. The measured results were compared with the measurements made previously with the same setup for C_2H_6-, C_2H_5OH- and C_2H_2-containing mixtures. It was shown that the effect of plasma on ignition is almost the same for C_2H_6, C_2H_4 and C_2H_5OH. The reduction in time is smaller for C_2H_2, the fuel that is well ignited even without the discharge. Autoignition delay time was independent of the stoichiometric ratio for C_2H_6 and C_2H_4, whereas this time in stoichiometric C_2H_2- and C_2H_5OH-containing mixtures was noticeably shorter than that in the lean mixtures. Ignition after the discharge was not affected by a change in the stoichiometric ratio
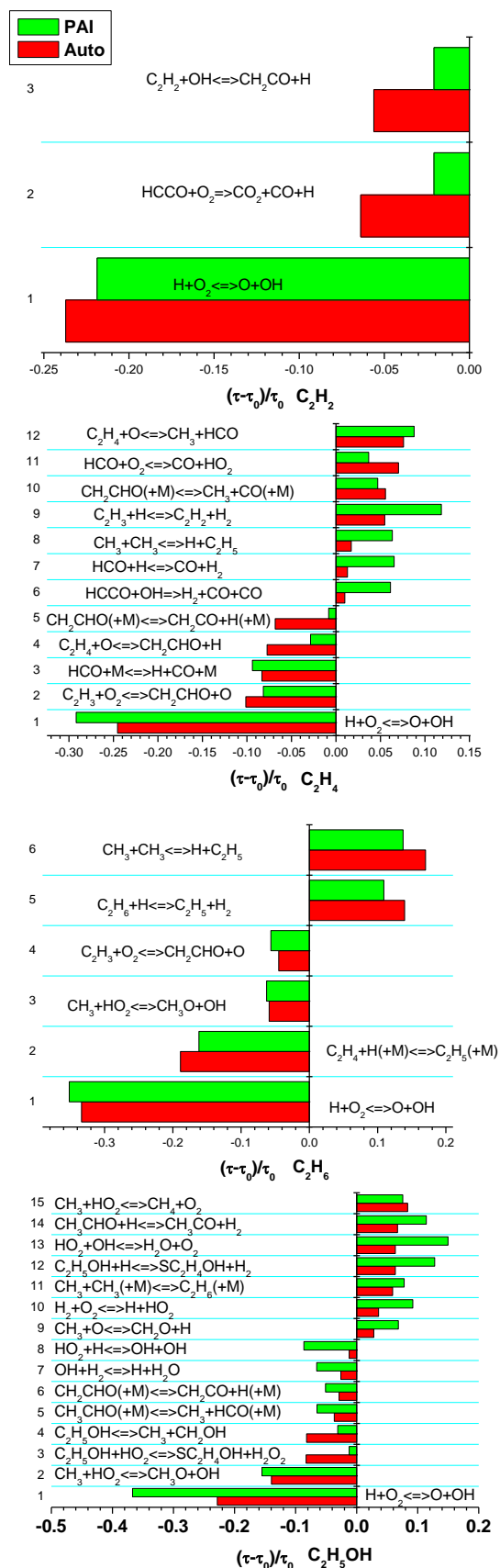
Fig. 3. Analyse of sensitivity for C_2H_2(a), C_2H_4 (b), C_2H_6(c) and C_2H_5OH (d), mixtures during autoignition and PAI at T=1300K and p=0.5 atm.

for C_2H_2 and C_2H_4, whereas the plasma-assisted

ignition delay time for C_2H_6 and C_2H_5OH decreased as the equivalence ratio changed from 1 to 0.5.

Ignition delay time was calculated in C_2-hydrocarbon-containing mixtures under study by simulating separately discharge and ignition processes. Good agreement was obtained between new measurements and calculated ignition delay times. Sensitivity analysis was used to show the peculiarities of ignition with and without the discharge for C_2-hydrocarbons under study.

5. Acknowledgements

6. References

[1] S.M. Starikovskaia, *J. Phys. D: Appl. Phys.* **39** (2006) 265.

[2] A.Yu. Starikovskiy, N.L. Aleksandrov, Prog. Energy Comb. Sci. **39** (2013) 61.

[3] S.M. Starikovskaia, *J. Phys. D: Appl. Phys.* **47** (2014) 353001.

[4] Y. Hidaka, Y. Tanaka, H. Kawano, M. Suga, *Mass Spectrom.* **29** (1981) 191.

[5] I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia, A.Yu. Starikovskii, *Comb. Flame* **156** (2009) 221.

[6] I.N. Kosarev, A.I. Pakhomov, S.V. Kindysheva, E.M. Anokhin, N.L. Aleksandrov, *Plasma Sources Sci. Technol.* **22** (2013) 045018.

[7] I.N. Kosarev, S.V. Kindysheva, N.L. Aleksandrov, A.Yu. Starikovskiy, *Comb. Flame* **162** (2015) 50.

[8] S.A. Bozhenkov, S.M. Starikovskaia, A.Yu. Starikovskii, *Comb. Flame* **133** (2003) 133.

[9] S.M. Starikovskaia, E.N. Kukaev, A.Yu. Kuksin, M.M. Nudnova, A.Yu. Starikovski, *Comb. Flame* **139** (2004) 177.

[10] I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia, A.Yu. Starikovskii, *Comb. Flame* **154** (2008) 569.

[11] G. Mittal, S.M. Burke, V.A. Davies, B. Parajuli, W.K. Metcalfe, H.J. Curran, *Comb. Flame* **161** (2014) 1164.